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Photoluminescence measurements from the two polar faces of ZnO

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The crystal structure of ZnO is wurtzite and the stacking sequence of atomic layers along the “ c ” axis is not symmetric. As a result, a ZnO crystal surface that is normal to the c axis exposes one of two distinct polar faces, with (000 $\bar{1}$) being considered the O face and (0001) the Zn face. Photoluminescence (PL) measurements on the two faces reveal a striking difference. Two transitions are observed in PL that are dominant from the O face and barely observed in PL from the Zn face. These lines are identified as phonon replicas of a particular D^0,X transition using energy separations, excitation dependence, and time-resolved PL measurements. In addition, PL emission from free excitons is found to be more intense from the O face than from the Zn face. © 2000 American Institute of Physics. [S0021-8979(00)02018-1]

I. INTRODUCTION

The crystal structure of ZnO is wurtzite, and the stacking sequences of atomic layers along the “ c ” axis are not symmetric. As a result, a ZnO crystal surface that is normal to the c axis exposes one of two distinct polar faces, with (000 $\bar{1}$) being considered the O face and (0001) the Zn face. The two faces are known to be structurally and chemically different.^{1,2} They have been identified by x-ray diffraction, low energy electron diffraction,³ photoelectron diffraction,⁴ coaxial impact-collision ion scattering spectroscopy,⁵ the sign of the piezoelectric coefficient, and etch rate measurements in HCl or H₂NO.⁶

In the current paper we compare photoluminescence (PL) measurements on the two polar faces of ZnO. Results from the two faces have much in common—the strongest emission comes from a set of lines associated with neutral-donor-bound excitation (D^0,X) complexes⁷—but there are two major differences. The most striking difference is observed at energies below those of the D^0,X complex lines: PL from the O face exhibits two lines whose PL intensity is dramatically reduced in PL from the Zn face. Energy separations, excitation dependence, and time-resolved PL measurements all suggest that these lines are phonon replicas of a particular D^0,X transition. The other major difference appears in spectra at energies above those of the D^0,X complexes. PL emission from free excitons is considerably more intense from the O face than from the Zn face.

II. EXPERIMENT

The ZnO sample was grown by a seeded physical vapor transport method. The c axis of the crystal is normal to the

growing surface. Temperature-dependent Hall effect measurements yielded a hydrogenic (60 meV) donor concentration N_D of $1 \times 10^{17} \text{ cm}^{-3}$, and a total acceptor concentration N_A of $2 \times 10^{15} \text{ cm}^{-3}$. Time-integrated photoluminescence spectra were measured at 2 K with the sample immersed in liquid He. PL excitation was provided by the 3250 Å line of a HeCd laser. The spectra were analyzed by means of a high resolution 4 m grating spectrometer equipped with an RCA C 31034A photomultiplier tube. Time-resolved photoluminescence measurements were made with a Hamamatsu model C1587 synchroscan streak camera. The excitation source was a frequency-tripled mode-locked Ti:sapphire laser producing pulses with a wavelength around 2750 Å and a nominal pulse width below 1 ps. Although the streak camera is capable of 10 ps resolution, trigger jitter and the narrow spectrometer bandwidth limited the effective temporal resolution to about 50 ps.

III. RESULTS

PL spectra from the O face of the ZnO sample are shown in Fig. 1(a) for various excitation intensities. The strong set of lines near 3.36 eV result from neutral-donor-bound excitation complexes (D^0,X) associated with defect pairs.⁷ The peak at 3.3779 eV is the free exciton emission. Note the strong excitation dependence of the 3.3622 eV line compared to that of other D^0,X lines—at the lowest exciting intensity, it is not even visible. PL spectra from the Zn face of the same sample are shown in Fig. 1(b). Except for a small shift in energy, the D^0,X lines behave similarly on both faces. In contrast, the free exciton lines observed in the O-face PL are *essentially absent* in the Zn-face PL. A more striking contrast in PL from the two faces is evident in Fig. 2, which

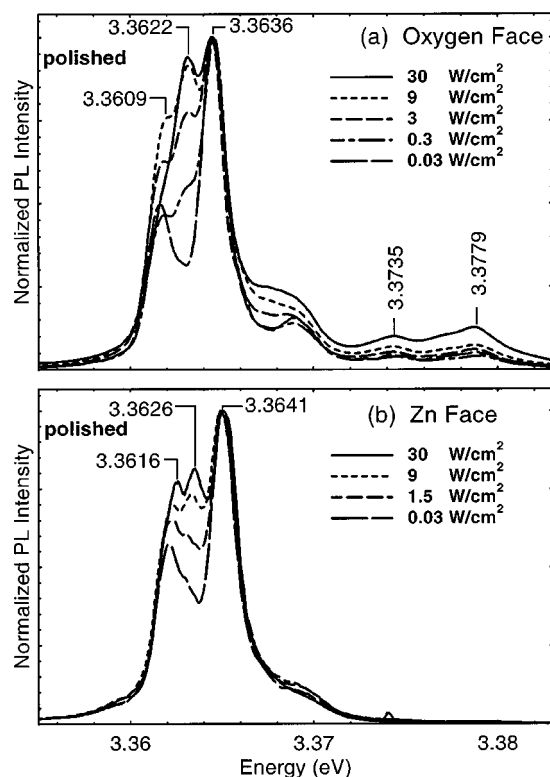


FIG. 1. Normalized ZnO photoluminescence spectra (above 3.35 eV) from (a) the O face and (b) the Zn face. Excitation intensities are given in the legends. The O-face spectra at the two highest excitation intensities exhibited small shifts in emission energy, possibly from band-renormalization effects. These shifts were removed for improved clarity: the 30 W/cm² spectrum was shifted by +0.59 meV, and the 9 W/cm² spectrum was shifted by +0.25 meV.

displays spectra for energies below 3.35 eV. The spectra from the O face in Fig. 2(a) display lines at 3.2367 and 3.3115 eV that are not evident in the spectra from the Zn face in Fig. 2(b). These lines also depend more strongly on excitation intensity than do the surrounding spectral features, reminiscent of the 3.3622 line in Fig. 1(a). To rule out the possibility that polishing damage may influence the PL differently from the two polar faces of ZnO, the polished faces were etched in concentrated HCl for 10 min. The strong excitation dependence of the line near 3.3622 eV for both the O face and the Zn face is still evident as shown in Figs. 3(a) and 3(b), respectively. At the lowest exciting intensity the line is missing from both faces as was the case for the polished faces. At longer wavelengths the lines at 3.3091 and 3.2342 eV are clearly dominant over the same energy positions on the Zn face as is seen in Fig. 4. This also follows the pattern observed for the polished faces. A cleaved Zn face was obtained and the spectral regions shown in Figs. 1(b) and 3(b) and 2(b) and 4(b) are repeated for the cleaved Zn face in Fig. 5. The spectral features are very similar for all three surface treatments giving evidence that the optical differences observed for the two polar faces of ZnO are intrinsic to the material. We were not successful in obtaining a cleaved O face since the preferred cleavage is parallel to the *c* axis in ZnO.

Since the 3.3622 eV line results from direct recombination of a particular D^0, X complex, we suggest that the

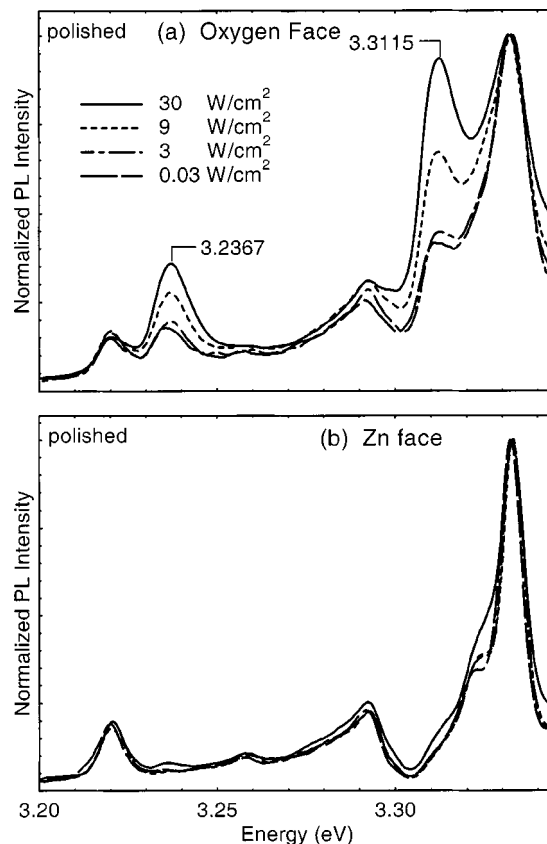


FIG. 2. Normalized ZnO photoluminescence spectra (below 3.35 eV) from (a) the O face and (b) the Zn face. The excitation intensities in the legend apply to both (a) and (b).

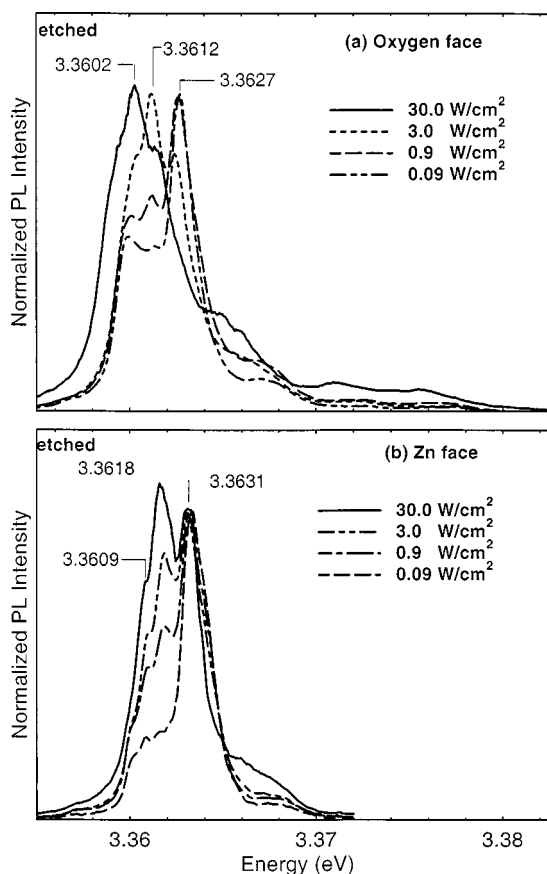


FIG. 3. Repeat of Fig. 1 for etched faces.

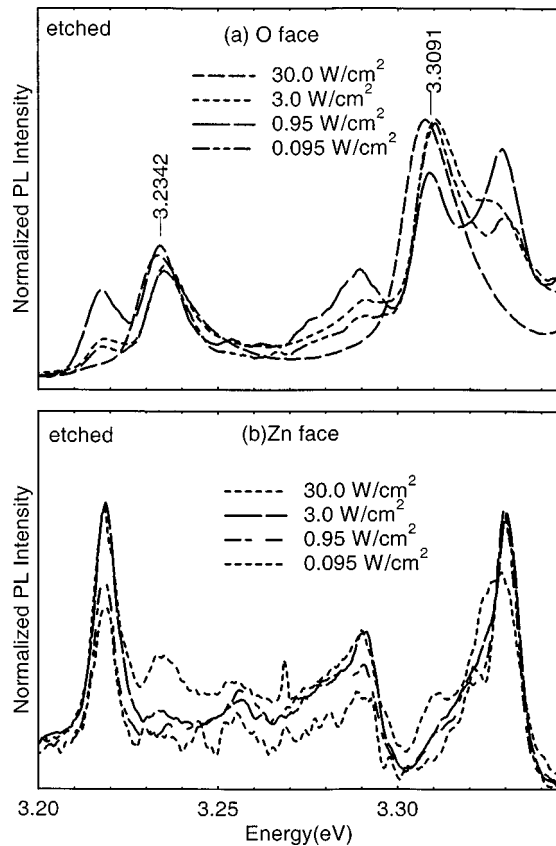


FIG. 4. Repeat of Fig. 2 for etched faces.

3.3115 eV line results from collapse of the same complex along with emission of an E_1 -TO phonon, and the 3.2367 eV line results from collapse of the complex with emission of both an E_1 -TO phonon and an E_1 -LO phonon. The observed energy separations imply energies of 50.7 meV for the E_1 -TO phonon and 74.8 meV for the E_1 -LO phonon, in close agreement with 50.5 and 72.3 meV obtained from Raman measurements.⁸ Curiously, no phonon replica is observed near 3.2874 implying that the D^0, X complex does not collapse and excite only a single E_1 -LO phonon. This may suggest that the coupling between the E_1 -LO phonon and the transverse exciton is weak.

Both reduced free-exciton emission and the absence of phonon replicas suggest that the local crystal environment near the Zn face is different from that near the O face. Perhaps the Zn face is more subject to atmospheric contamination than the O face. The resulting surface state defects could lead to band tailing that would absorb the near-band-edge free-exciton emission. The fact that PL from the Zn face clearly exhibits the parent D^0, X transition [Fig. 1(b)] but *not* the phonon replicas [Fig. 2(b)] indicates that either the D^0, X transition cannot couple to phonons near the Zn face, or the requisite phonons are not supported near the Zn face.

To further verify the identification of the phonon replicas, time-resolved PL was used to measure the decay lifetimes for the 3.3622, 3.3115, and 3.2367 eV lines. Results are shown in Fig. 6. The data display single exponential decays for all of the transitions over several times the radiative recombination lifetime. Decay times were obtained from

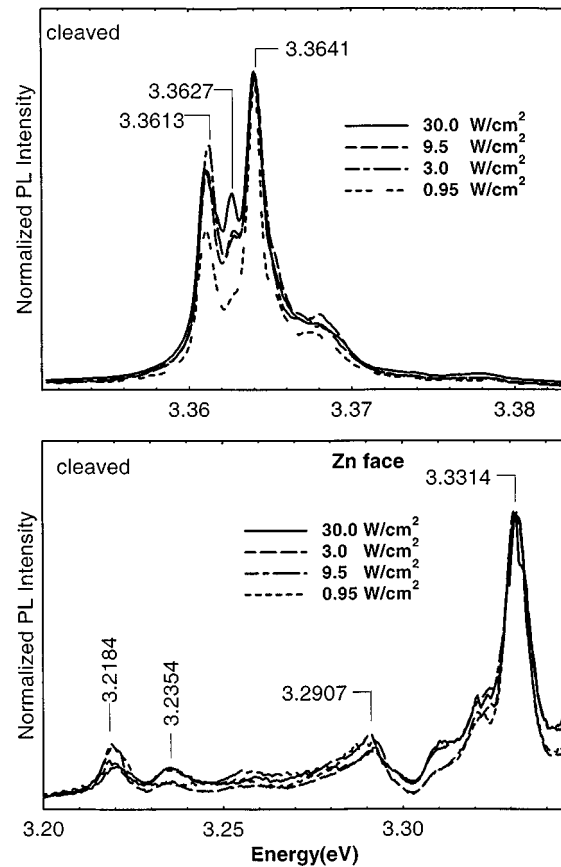
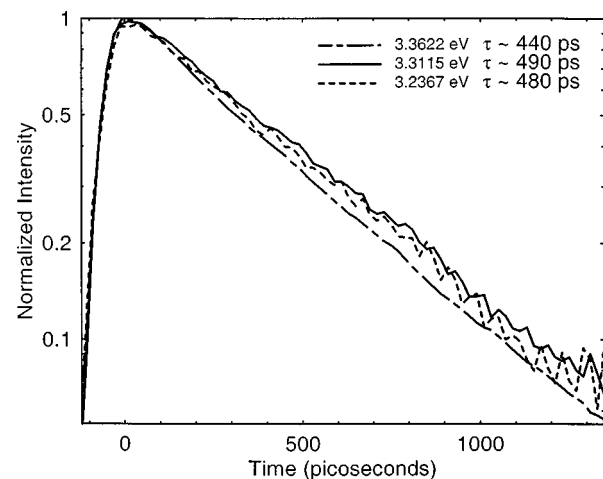


FIG. 5. Repeat of Figs. 1(b) and 3(b) and 2(b) and 4(b) for the Zn cleaved face.

a least-squares fit of the data to a single exponential for intensities between 0.85 and 0.05. The decay time for the D^0, X transition at 3.3622 eV was 440 ps while the decay times for the phonon replicas at 3.3115 and 3.2367 eV were 490 and 480 ps, respectively. Since the phonon replicas presumably result from low-probability decay branches for the D^0, X state, one would expect their intensities to track the decaying D^0, X state population. This would make the replica decay lifetimes match the parent transition lifetime, as is observed.

FIG. 6. Time-resolved photoluminescence intensity decays for the D^0, X line at 3.3622 eV and its phonon replicas at 3.3115 and 3.2367 eV.

IV. CONCLUSION

We have measured photoluminescence (PL) spectra from the polar faces of ZnO. Distinct differences were observed. PL from the O face exhibits two transitions that are clearly dominant over transitions from the same two energy positions with respect to the Zn face. Using energy separations, excitation dependence, and time-resolved PL measurements, these lines are identified as phonon replicas of a particular D^0, X transition. In addition, PL emission from free excitons is considerably more intense from the O face than from the Zn face. These features observed for three different surface treatments points to their intrinsic nature.

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